J Paleolimnol (2009) 41:563–588
DOI 10.1007/s10933-008-9292-5

ORIGINAL PAPER

Historical changes in sediment and phosphorus loading to the upper Mississippi River: mass-balance reconstructions from the sediments of Lake Pepin

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Received: 15 April 2007 / Accepted: 1 February 2008 / Published online: 15 January 2009

Abstract Long-term changes in sediment and phosphorus loading to the upper Mississippi River were quantified from an array of 25 sediment cores from Lake Pepin, a large natural impoundment downstream of the Minneapolis-St Paul metropolitan area. Cores were dated and stratigraphically correlated using ^{210}Pb, ^{137}Cs, ^{14}C, magnetic susceptibility, pollen analysis, and loss-on-ignition. All cores show a dramatic increase in sediment accumulation beginning with European settlement in 1830. Accumulation rates are highest and show the greatest post-settlement increases in the upper end of the lake. Present-day sediment-phosphorus concentrations are roughly twice those of pre-settlement times, and the Fe/Al-bound fraction makes up a greater portion of the total. Diatom assemblages record a marked increase in nutrient availability over the last 200 years, changing from clear-water benthic forms and mesotrophic planktonic taxa in pre-settlement times to exclusively planktonic assemblages characteristic of highly eutrophic conditions today. Lake-water total-phosphorus concentrations, estimated by weighted averaging regression and calibration, increased from 50 to 200 μg l^{-1} during this period. Sediment loading to Lake Pepin from the Mississippi River has increased by an order of magnitude since 1830. Modern fluxes are about 900,000 metric tons annually, and are more than 80% detrital mineral matter. About 17% of the lake's volume in 1830 has been replaced by sediment, and at current accumulation rates the remainder will be filled in another 340 years. Phosphorus accumulation in Lake Pepin sediments has increased 15-fold since 1830, rising from 60 to 900 metric tons annually. This rise represents a sevenfold increase in phosphorus loading from the Mississippi River coupled with more efficient retention of phosphorus inflows by bottom sediments. More efficient trapping of phosphorus in Lake Pepin over the last century resulted from higher rates of sediment burial. The most dramatic changes in nutrient and sediment inputs to Lake Pepin have occurred since 1940, although gradual increases began shortly following European settlement. Sediment accumulation rates rose sharply between 1940 and 1970 and then leveled off, while phosphorus inflows record their largest increases after 1970.

Keywords Mississippi River · Lake Pepin · Sediment accumulation · Phosphorus loading · Diatoms · Lead-210 dating

This is one of eight papers dedicated to the "Recent Environmental History of the Upper Mississippi River" published in this special issue of the Journal of Paleolimnology. D. R. Engstrom served as guest editor of the special issue.

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Introduction

The Mississippi is the largest and economically most important river in North America. It drains 40% of the conterminous United States and carries each year an estimated 0.14×10^6 metric tons (t) of P, 1.5×10^6 t of nitrogen and 150×10^6 t of suspended sediment to the Gulf of Mexico (Goolsby et al. 1999, 2001). These loads have increased within recent decades resulting in eutrophication of the continental shelf and areal expansion of summer hypoxia in the northern Gulf (Rabalais et al. 2002a, b; Turner and Rabalais 1994). Impaired water quality is an equally serious concern for the upper Mississippi River (UMR), where a combination of point and non-point sources of phosphorus (P) have created highly eutrophic conditions that in 1988 caused severe algal blooms and fish kills downstream of the Minneapolis-St Paul (Twin Cities) metropolitan area (Heiskary and Vavricka 1993; MWCC 1993d). These concerns are heavily focused on Lake Pepin, a large natural impoundment of the Mississippi below the Twin Cities and an important recreational and commercial resource for the region. Lake Pepin was recently the subject of a major inter-agency water-quality study designed to quantify impacts of point and non-point P loads within the basin (MWCC 1993a). A key element of that study, on which we report here, is the historic assessment of long-term changes in sediment and P loading to the Mississippi above Lake Pepin. This information is critical to understanding the extent of the eutrophication problem compared to natural background conditions and for determining present rates of change and future projections for the river (Smol 1992).

Historic water quality data, even for a river of the Mississippi's stature, are of relatively short duration. Reliable estimates of nutrient loads to Lake Pepin, which go back to the early 1970s, suggest a steady increase in P inputs (adjusted for flow variations) over the last two decades (Heiskary and Vavricka 1993). Earlier records are sparse to non-existent, and long-term change instead must be inferred from sediments accumulated in depositional environments along the Mississippi's course. Rising concentrations of biogenic (diatom) silica, phytoplankton pigments, marine-origin carbon, and other geochemical indicators in sediment cores from the Gulf coast provide strong evidence for twentieth century eutrophication by the Mississippi River (Rabalais et al. 2007), but such information is largely qualitative (regarding actual nutrient loads) and cannot be applied to specific upstream reaches. With few exceptions, there is little historical evidence for eutrophication of the world's major rivers, though most are considered to be highly impacted by human activities in their watersheds (Turner et al. 2003). The major problem is that most rivers do not possess along their course depositional basins where sediments accumulate conformably, and in this respect Lake Pepin is nearly unique. In this investigation we compile, through analysis of multiple sediment cores, a quantitative estimate of sediment and P loading to the UMR over the last several hundred years.

Lake sediment cores have been used in numerous studies to produce qualitative estimates of past trophic state, the most common proxies being the accumulation rate of P and the composition of fossil diatom assemblages. Both approaches have become more quantitative in recent years, with whole-basin P accumulation now calculated from multiple sediment cores (Brezonik and Engstrom 1998; Evans and Rigler 1980; Moss 1980), and lakewater P concentrations numerically reconstructed by multivariate transfer-function techniques (Anderson and Rippey 1994; Bennion 1994; Hall and Smol 1992). In an elegant synthesis of these methods, Rippey and Anderson (1996) demonstrated that historical P loadings to lakes could be rigorously determined from a mass-balance sum of P sedimentation and outflow [the latter calculated from historic flows and diatom-inferred lake-water total-P (TP)]. The major advantage of this mass-balance approach (over diatoms or sediment-P alone) is that P sedimentation is strongly influenced by redox changes that accompany eutrophication (Engstrom and Wright 1984; Schelske et al. 1988) as well as changes in hydraulic residence time which are pronounced in riverine lakes like Pepin. Hence, we adopt in this study a combination of diatom-inference and whole-lake sedimentation methods to provide the first quantitative account of human alteration of P and sediment loads to one of the world's great rivers.

Study area

Lake Pepin is a natural floodplain lake on the UMR located about 80 km downstream from the Twin Cities metropolitan area of Minnesota. The lake formed about 10,000 years ago behind an alluvial fan of the Chippewa River, which dammed the Mississippi after outflow from Glacial Lake Agassiz was diverted northward and ceased to scour sediments deposited by the Mississippi's tributaries (Blumentritt et al. this issue; Wright et al. 1998). Although much larger in the distant past, Lake Pepin today has a length of 34 km, a mean depth of 5.4 m, and a surface area of 103 km^2 (Fig. 1). Mean annual flows of the Mississippi River above Lake Pepin are about 600 m^3 s^{-1} (Stark et al. 1996), and residence time in the lake is relatively short (6–47 days) (Heiskary and Vavricka 1993). Water quality in Lake Pepin today is generally poor, reflecting the combined impacts of urban and agricultural developments upstream. Mean summer TP concentrations at the inflow to Lake Pepin averaged 215 µg l^{-1} and total suspended solids concentrations averaged 41 mg l^{-1} between 1977 and 1991 (Heiskary and Vavricka 1993).

The Mississippi River above Lake Pepin drains about 122,000 km^2, mostly in Minnesota and adjacent Wisconsin, through many small tributaries and two major rivers, the Minnesota and St Croix (Fig. 1). These two tributaries each provide about one-fourth of the mean annual flow entering Lake Pepin, although the Minnesota's watershed is more than twice that of the St Croix (Stark et al. 1996). Precipitation and runoff are substantially higher in the eastern regions drained by the St Croix. The watershed of the Minnesota is 85–90% agricultural, (predominately row crops), and presently contributes 75% of the suspended solids and 32% of the P loads to the UMR above Lake Pepin in an average flow year (MWCC 1993b, 1994). The St Croix's watershed, on the other hand, is largely forested and provides only about 4% of the average P inputs to the UMR above Lake Pepin. The watershed of the Mississippi main stem is forested in the north, grading to agricultural (pasture and dairy) in the south; it provides about 26% of the P loads to the UMR. The Minneapolis-St Paul urban area (1990 population of 2.3 million) contributes about 24% of the remaining P loads (under average flow conditions) through its waste-treatment facilities, while other point-source discharges and smaller tributaries make up the difference (MWCC 1993b).

Methods

Sediment coring

A total of 25 sediment cores were collected (September 1995, and June and October 1996) along five shore-to-shore transects positioned perpendicular to the flow axis of Lake Pepin (Fig. 1). The transects

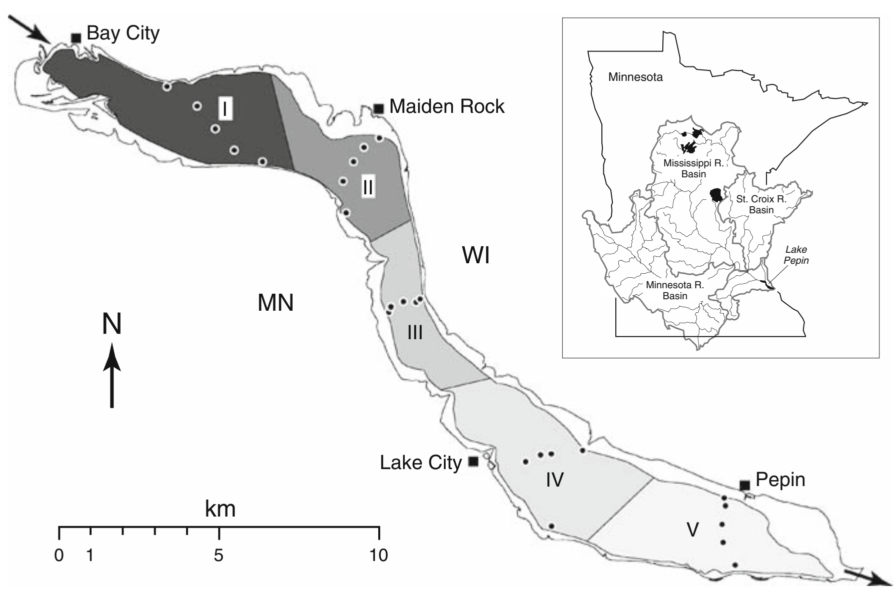


Fig. 1 Location of core sites and depositional regions in Lake Pepin. *Inset map* shows major sub-basins of the upper Mississippi River above Lake Pepin

were distributed at roughly equal distances from upper to lower reaches of the lake, and five cores were taken along each transect. Cores are designated here by transect number (I–V from upper to lower lake) and position along the transect (1–5 from the Minnesota to the Wisconsin side of the Lake); for example core V.1 is from the lowermost transect closest to the Minnesota side. Core locations were recorded in the field by differential GPS. Additional reconnaissance cores were collected to help delineate the depositional limit of fine-grained sediments in Lake Pepin; these cores were discarded in the field.

Sediments were collected during the open-water season using piston corers operated from the lake surface by rigid drive-rods. A surface corer equipped with a 7-cm diameter polycarbonate core barrel was used to collect a continuous 2-m section of the upper sediments at all coring sites (Wright 1991). This device recovers the watery, uncompacted sediment surface as well as deeper strata without disturbance or displacement (core-shortening) (Blomqvist 1985, 1991). Additional 1-m overlapping drives were taken below the surface core-section with a square-rod Livingstone corer (Wright et al. 1983) at those sites where very rapid sediment accumulation was anticipated (transects I–III); total core length at these locations was 3.5–4 m. The surface core-sections were held upright until the upper 20–24 cm of soft sediment could be extruded vertically (at 2-cm increments) into polypropylene collection jars on shore. The remaining section of stiff sediment was capped in the core tube and transported back to the lab in horizontal position. The Livingstone sections were extruded on site and wrapped in polyethylene film (food-wrap) and aluminum foil. The cores were stored at 4°C until further processing.

Mapping

Core locations, seismic-survey routes, bathymetric data, and geographic reference points for Lake Pepin were precisely mapped using ArcInfo GIS technology. Rasterized bathymetric data, provided by the USGS Environmental Management Technical Center, Onalaska, WI, were contoured at 1-m intervals and used together with reconnaissance coring and seismic results to delineate depositional regions for fine-grained sediment. Throughout much of Lake Pepin the depositional limit (above which fine-grained sediments do not accumulate) corresponds closely to a sharp bathymetric scarp separating shallow nearshore areas from a generally flat central basin. Hence, the depositional limit could be mapped along this scarp everywhere except in the shallow upper end of the lake where the limit was approximated at the middle of the 1-m contour. The total depositional area of Lake Pepin was subdivided into five depositional regions, one for each transect of cores, by the perpendicular bisector between adjacent transects (Fig. 1).

Magnetic susceptibility

For all 25 cores, whole-core magnetic susceptibility measurements were made at 2-cm intervals using a Bartington MS2 core logging sensor and automated track. These measurements provide a non-destructive determination of the concentration of fine-grained ferromagnetic minerals within the sediments. Cores were measured in 1-m sections, and magnetic profiles were spliced between sections according to sediment depth. In some cores it was necessary to make depth adjustments of a few centimeters between overlapping sections to align magnetic features. Susceptibility readings for the smaller diameter Livingstone core-sections were scaled to those of the surface core-sections before splicing records.

Core sampling

Following measurement of whole-core magnetic susceptibility, ten of the 25 cores were selected for detailed stratigraphic analysis (two per transect) and were subsectioned into 4-cm increments. Each core-section was scraped with a stainless steel spatula to remove the outside smear and subsectioned with a thin wire. In most cases, only the surface core-section was completely subsampled; the 1-m Livingstone core-sections were stored intact and only selected 4-cm increments were removed for analysis. An additional 10 cores were chosen for “top/bottom” stratigraphic analysis in which constituents were analyzed from just two time-stratigraphic intervals. Core-top samples ranged in length from 12 to 24 cm (depending on sedimentation rate) and represented on average the last 7 years of sediment deposition. Core-bottom samples, 4–15 cm in length, were taken from strata deposited just prior to European settlement and represented an average accumulation of 60 years.

Loss-on-ignition

Dry-density (dry mass per volume of fresh sediment), water content, organic content, and carbonate content of Pepin sediments were determined by standard loss-on-ignition (LOI) techniques (Dean 1974). Sediment samples of 1–2 g were dried overnight at 100°C and ignited at 550 and 1,000°C for 1 h each. Mass measurements were made of the wet samples and after each heating on an electronic analytical balance. Dry density was calculated from water content and fixed densities for organic, carbonate, and inorganic fractions.

Pollen analysis

Pollen samples from five cores were prepared according to procedures described by Faegri and Iversen (1975). A known quantity of *Eucalyptus* pollen was added to selected samples as a tracer to permit calculation of pollen concentration. Residues were mounted in silicon oil, and pollen identified under magnifications of 400× and 1,000×. At least 300 terrestrial pollen grains were counted in each sample.

Radiocarbon dating

Small pieces of terrestrial woody material were sieved from a selected depth interval in each of two cores. The selected intervals corresponded to magnetic features identifiable in many of the other cores. Samples were washed in deionized water, dried, and submitted to the Limnological Research Center of the University of Minnesota for graphite target preparation. The targets were analyzed by accelerator mass spectrometry (AMS) at the Center for Accelerator Mass Spectrometry of the Lawrence Livermore National Laboratory. Radiocarbon dates were converted to calendar years AD using the CALIB program of Stuiver and Reimer (1993) and calibration data sets from Stuiver and Pearson (1993).

Cesium-137 dating

Twenty sediment cores were analyzed for ^{137}Cs to identify sediments deposited during the 1963–1964 peak in atmospheric nuclear testing. Freeze–dried samples (ca. 20 g) were measured for ^{137}Cs at 667 keV using a high-resolution germanium diode gamma detector and multichannel analyzer. Detector efficiency was around 2% as determined using a NIST-certified source with mineralogical composition similar to the samples (Rocky Flats soil/SRM4353). Accuracy and precision were better than 10% for a 12 h measurement of concentrations of $\sim$30 Bq kg^{-1}.

Lead-210 dating

Ten sediment cores were analyzed for ^{210}Pb activity to determine age and sediment accumulation rates for the past 130 years. Lead-210 was measured at 17–24 depth intervals in each core through its granddaughter product ^{210}Po, with ^{209}Po added as an internal yield tracer. The polonium isotopes were distilled from 1.5–7.0 g dry sediment at 550°C following pretreatment with concentrated HCl and plated directly onto silver planchets from a 0.5 N HCl solution (Eakins and Morrison 1978). Activity was measured for 1–3 × 10^5 s with ion-implanted or Si-depleted surface barrier detectors and an Ortec alpha spectroscopy system. Unsupported ^{210}Pb was calculated by subtracting supported activity from the total activity measured at each level; supported ^{210}Pb was estimated from the asymptotic activity at depth (the mean of the lowermost samples in a core). Dates and sedimentation rates were determined according to the c.r.s. (constant rate of supply) model with confidence intervals calculated by first-order error analysis of counting uncertainty (Appleby 2001).

Phosphorus analysis

Samples from 20 sediment cores were extracted for P according to fractionation procedures adapted from Hieltjes and Lijklema (1980) and Plumb (1981). Total-P was measured as the ortho-P extracted by block-digestion with concentrated H_2SO_4, K_2SO_4, and HgO. A second sediment aliquot was extracted in 1 M NH_4Cl for exchangeable-P (NH_4Cl-P), followed sequentially by 0.1 M sodium hydroxide for Fe/Al-bound P (NaOH-P). The sediment residue from the hydroxide extraction was further treated with 0.5 M HCl to determine carbonate-bound P (HCl-P). Finally the residual (organically bound) P was estimated as the difference between TP and the sum of the NH_4Cl, NaOH, and HCl extractions. Extractions were carried out on wet sediment samples, and water content was measured simultaneously on separate aliquots. Extracts were separated from sediment residue by centrifugation and membrane filtration. Phosphorus extracts were analyzed for ortho-P by the ascorbic acid method. Standard absorbance curves were constructed from an analytical P-standard in the appropriate matrix for each fraction. The reproducibility of sample replicates averaged 2.9% for TP, 9.2% for NH_4Cl-P, 5.2% for NaOH-P, and 4.6% for HCl-P.

Diatom analysis

Ten subsamples from core V.1 were analyzed for diatom microfossils. Normal cleaning procedures with H_2O_2 or sulfuric acid were not adequate for these sediments because of their high silt content. As an alternative method, uncleaned sediment samples were diluted with distilled water, settled, and dried overnight onto cover slips. The dried samples were then heated at high temperature to remove any organic matter. Coverslips were mounted on slides with Naphrax. Diatom valves and chrysophyte cysts were counted in transects with a Leitz Ortholux microscope at 1,200× magnification under oil immersion. A minimum of 500 diatom valves were counted in each sample except where diatom concentrations were very low. In these cases, a minimum of 400 valves or six transects were counted.

Lake-water TP was reconstructed from fossil diatom assemblages using diatom-P calibration models. Such models are developed using canonical correspondence analysis (CCA) and weighted averaging regression on the distribution of diatom species among lakes of known water chemistry (Birks et al. 1990; ter Braak and Prentice 1988). All taxa composing more than 1% in any one sample were selected for TP reconstruction. Some taxa were further eliminated if TP optima were not available from the literature and they composed <5% in any one sample. Several published calibration data sets for TP reconstruction in lacustrine systems were tested on the Lake Pepin data, as no calibration data set is presently available for large rivers. Among those tested was a data set of 80 Minnesota lakes (expanded from Ramstack et al. 2003). Unfortunately, this local calibration set is truncated at high TP values and was thus unable to reconstruct the high nutrient levels in present-day Lake Pepin ($\sim$200 μg P l^{-1}).

Although Lake Pepin is essentially a riverine system, the flora is primarily composed of lacustrine diatoms (predominately *Aulacoseira* and *Stephanodiscus* species) that are well represented in most lake-based calibration data sets. The majority of species optima used for the Lake Pepin analysis were obtained from a calibration set of 31 southeast English lakes (Bennion 1994) with TP values of 25–646 μg l^{-1}. This set was chosen because it represents high-nutrient systems similar to Lake Pepin. Because some low-nutrient taxa present in Lake Pepin are absent or poorly represented in Bennion (1994), additional species optima were obtained from Reavie et al. (1995). This second calibration set is based on 59 lakes in British Columbia with a TP range of 5–85 μg l^{-1}.

Results

Magnetic susceptibility

Whole-core magnetic susceptibility profiles show a striking pattern of peaks and troughs that can be readily traced among cores within each transect and, for the stronger features, from transect to transect throughout the lake basin (Fig. 2). The features were provisionally matched among profiles and numbered sequentially down-core. Subsequent dating analyses showed that the major magnetic features are time-synchronous and thus can be used to map time-stratigraphic units throughout the lake. Magnetic susceptibility, which is largely dependent on the concentration and size of magnetic mineral grains, is generally higher in the upper end of the lake and decreases downstream. Magnetic profiles in cores from the upper lake also show greater stratigraphic resolution than profiles from the lower lake, largely because of higher sediment accumulation rates in the upper lake. For example, magnetic feature (mf) 2 is a well defined trough in transects I and II but becomes a nearly imperceptible notch in transects IV and V. Likewise mf-4 and -6 are well separated peaks in transects I–III that become fused into a single peak in most of the transect V cores.

Magnetic feature 7 marks the initial rise in susceptibility from a low baseline and is the earliest

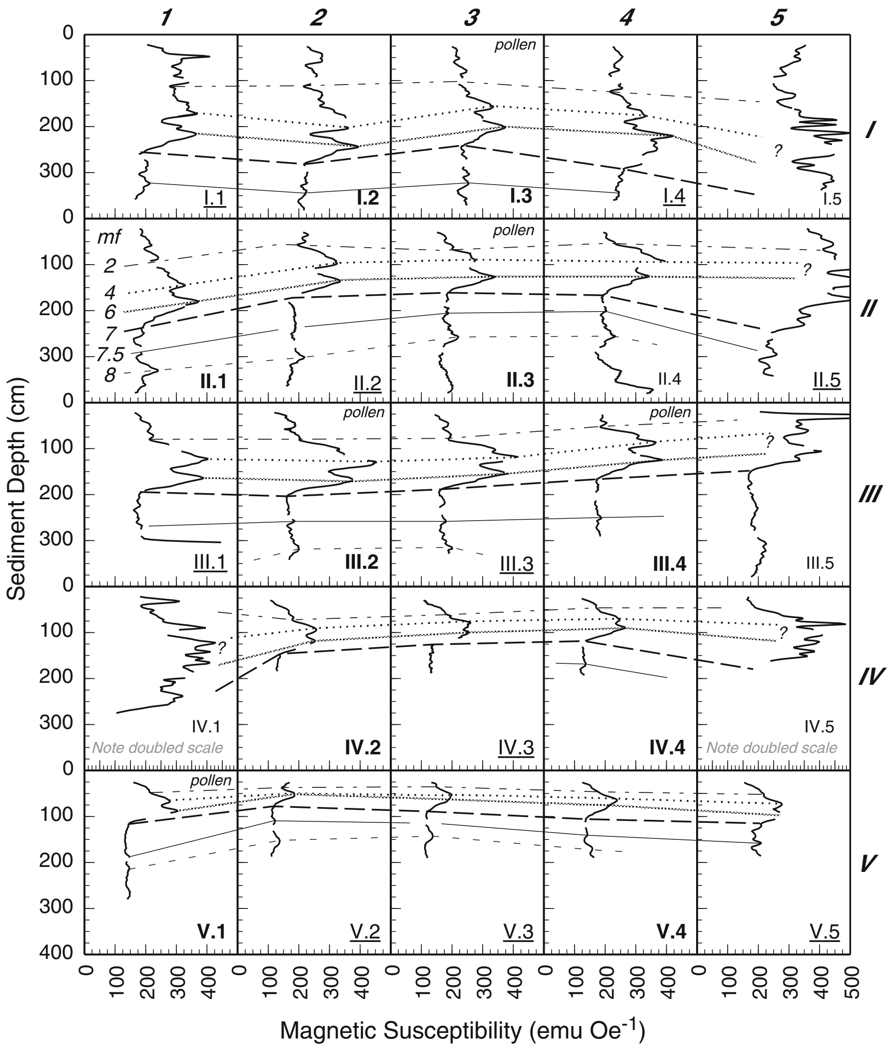


Fig. 2 Magnetic susceptibility profiles for all cores; correlated magnetic features (mf) indicated by *connecting lines*; cores selected for detailed stratigraphic analysis in **bold** type; cores selected for top/bottom analysis underlined; cores selected for pollen analysis as noted

stratigraphic evidence for European-settlement land-use changes in the upper Mississippi watershed (see dating section). A sharp rise in magnetic susceptibility is commonly associated with increased soil erosion caused by forest clearance and tillage agriculture (Dearing et al. 1981; Oldfield et al. 1978, 1989). Two small pre-settlement magnetic peaks (mfs-7.5 and -8) are identified in a smaller subset of cores (Fig. 2). Although these features are relatively easy to trace within transects, their correlation between core transects requires additional evidence from pollen analysis. A positive match of mf-7.5 is possible because this feature is associated with an increase in "big woods" vegetation (mesic hardwoods) in all five cores counted for pollen. Magnetic feature 8 has no clear pollen marker, except that it precedes the "big woods" change, so its correlation among transects is more tentative.

Magnetic susceptibility was used as a reconnaissance tool to select which cores would be analyzed in stratigraphic detail (two from each transect) and which would be analyzed for top (modern) and bottom (pre-settlement) samples (Fig. 2). A few magnetic profiles (I.5, III.5, IV.1 and IV.5) were difficult to match with the others and were excluded from subsequent analysis. All such problematic cores were taken from sites very near the steep bathymetric scarp at the sides of the channel where depositional discontinuities such as slumping or scouring are most likely. These core sites were selected to explore sediment stratigraphy in "atypical" depositional environments and likely represent only a small proportion of the lake bottom.

Loss-on-ignition

The percentages of organic matter, calcium carbonate, and inorganic matter in Lake Pepin sediments vary stratigraphically as well as spatially within the basin (Fig. 3). Organic matter averages 8.3% for all cores, but is lower at the upper end of the lake (7.3% in transect I) and increases progressively down lake (to 9.3% in transect IV). Carbonate content, on the other hand, shows the opposite pattern, decreasing from 12.8% in transect I to 8.3% in transect V. The inorganic component, largely comprised of clastic silicates, makes up the remaining 81% of the sediment and shows no longitudinal trend.

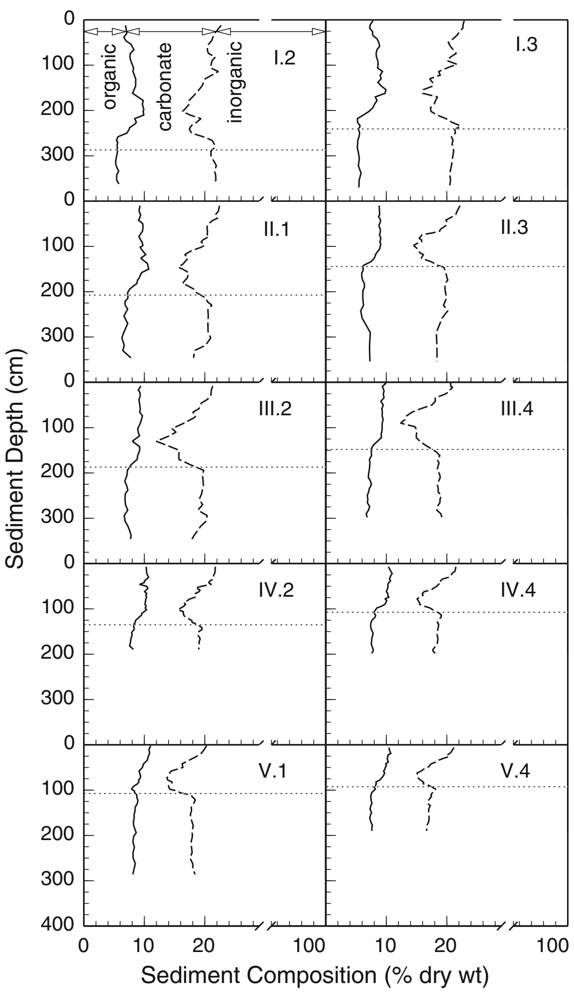


Fig. 3 Loss-on-ignition profiles for 10 detailed cores; sediment depths corresponding to settlement horizon (*Ambrosia* rise) indicated by *dashed lines*

More striking, however, is the sharp up-core increase in organic matter (2–4%) and inorganic constituents (4–6%) and corresponding drop in carbonate (6–10%) that occurs in all 10 cores analyzed in stratigraphic detail (Fig. 3). This transition occurs at greater core depth in the upper lake (deeper than 2 m in transect I) and at shallower depths in lower lake cores (about 1 m in transect V). The organic-matter increase is most pronounced in transect I, but the inorganic rise is equally sharp in all parts of the basin. Organic matter remains elevated from this transition to the sediment surface, while inorganic content peaks and then declines (as carbonate increases) toward the tops of the cores. In each core the LOI transition corresponds exactly to a point mid-depth between mfs-6 and -7 in the magnetic susceptibility profiles. The LOI change is also precisely correlated with pollen evidence for the onset of European-style agriculture and likely records increased soil erosion that accompanied widespread land clearance and watershed disturbance in the mid-1800s.

Pollen analysis

Pollen profiles constructed for five of the ten detailed cores reveal a clear stratigraphic change from a pre-settlement assemblage dominated by pine (*Pinus*), oak (*Quercus*), birch (*Betula*), and mesic hardwoods (big woods) to one with dramatically increased percentages of weedy herbaceous taxa, particularly ragweed (*Ambrosia*) and chenopods (Chenopodiaceae), the first appearance of cereal pollen grains (corn, wheat, etc.), and a sharp reduction in pine pollen (Fig. 4). This transition represents the rapid spread of European-style agriculture in southern Minnesota and adjacent Wisconsin and the near-simultaneous logging of local pine forests along the lower St Croix River. The exact timing of this "*Ambrosia* rise" is difficult to fix for a watershed the size of that contributing to Lake Pepin, but it is likely associated with the onset of large-scale commercial agriculture, which began around the time of Minnesota statehood (1858). The *Ambrosia* rise coincides stratigraphically in each core with LOI evidence for sharply increased erosion, indicating that landscape disturbance had become fairly widespread by this time. However, both of these changes (pollen and LOI) are preceded by an earlier rise in magnetic susceptibility that likely records the earliest phases of

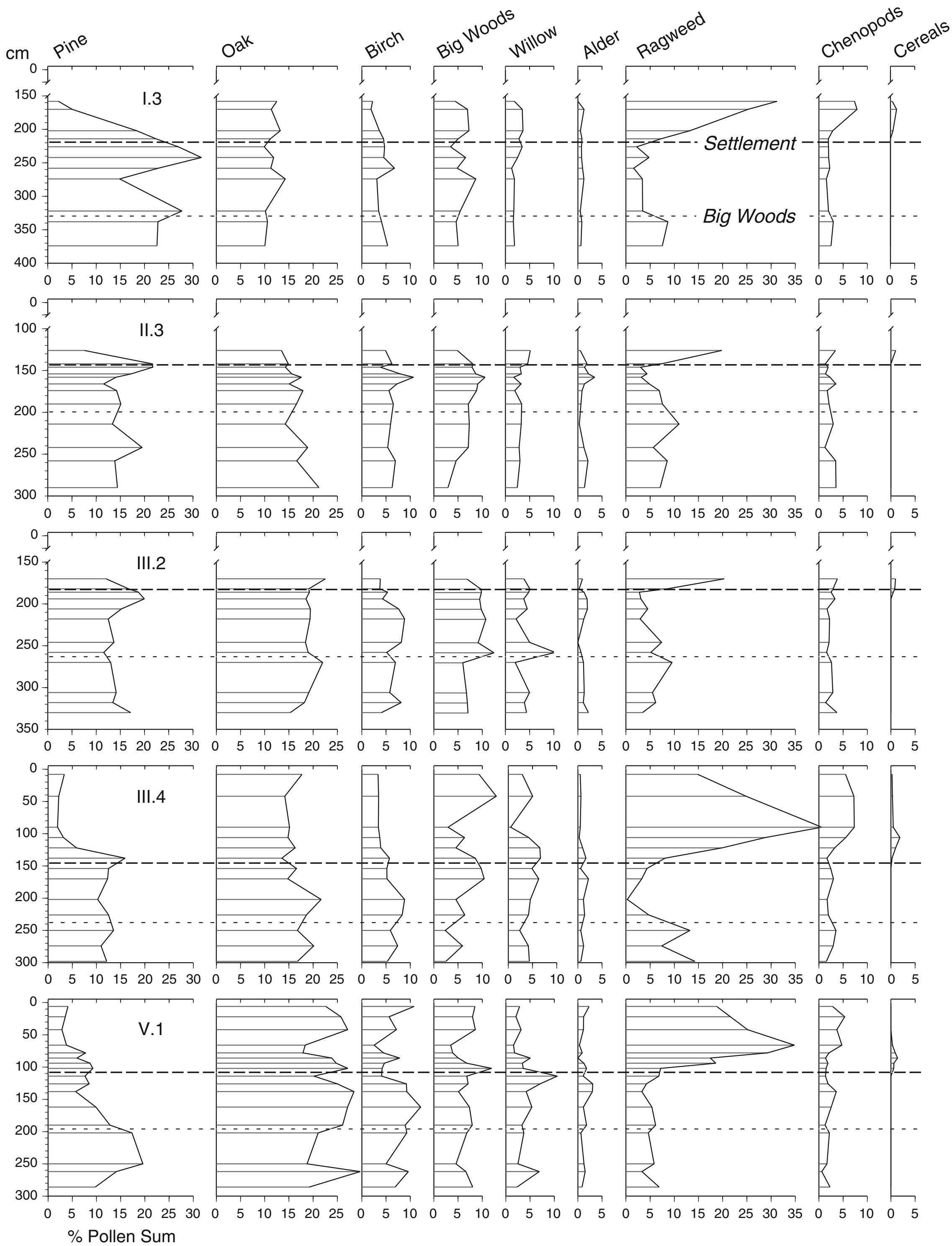


Fig. 4 Pollen percentage diagrams showing selected taxa for five detailed cores; approximate depths of settlement horizon (*Ambrosia* rise) and "big-woods" transition shown as *dashed* and *dotted lines*, respectively

European settlement and land-clearance in the Lake Pepin watershed (Fig. 2). The timing of this earlier magnetic marker is also uncertain, but a date of 1830, shortly following the establishment of Fort Snelling (at the confluence of the Minnesota and Mississippi rivers), is a reasonable first estimate. Both dates, 1860 for the Ambrosia rise and 1830 for the susceptibility increase, have an uncertainty of roughly ±10 years.

The sediments of Lake Pepin record a more subtle change in pollen composition that appears about a meter below the Ambrosia rise and at the same depth as mf-7.5 in the five analyzed cores (Fig. 4). The most important signature of this shift is the increase in "big woods" pollen types (*Acer*, *Tilia*, *Ulmus*, *Fraxinus*, *Ostrya/Carpinus*, and *Carya*); ragweed and other herbaceous taxa decline at this transition, while birch, willow (*Salix*) and alder (*Alnus*) show less consistent changes. These palynological changes are clearest in cores II.3, III.2, and III.4, and less obvious in cores I.3 and V.1. This pollen horizon is identified with the regional expansion of "big woods" vegetation that accompanied the onset of cooler, wetter climatic conditions several hundred years before European settlement (Grimm 1984). Although the timing of this vegetation change is somewhat uncertain, the pollen horizon itself provides a means of confirming stratigraphic correlation among cores in Lake Pepin. In particular it provides positive identification of mf-7.5 in susceptibility profiles among widely spaced core transects.

Radiocarbon dating

Two AMS ^{14}C dates, obtained on small woody macrofossils (about 10 mg each) in two separate cores, provide similar estimates of pre-settlement sedimentation rates in Lake Pepin. The dates, 400 ± 50 ^{14}C year. BP (CAMS-39310) and 740 ± 50 ^{14}C year. BP (CAMS-39311) occur at sediment depths of 261 cm in core III.2 and 327 cm in core II.1. These depths correspond, respectively, to magnetic susceptibility features (mf) 7.5 and 8. Calibration to a calendrical time-scale (Stuiver and Reimer 1993) yields dates of 1,473 (1,443–1,621; 1 sigma) for mf-7.5 (core III.2) and 1,284 (1,261–1,295; 1 sigma) for mf-8 (core II.1); the larger uncertainty for the younger date results from multiple intercepts of the ^{14}C calibration curve. Age-depth profiles for each of the two dated cores show fairly constant sediment accumulation rates between calibrated ^{14}C dates and dated mfs-7, -7.5 and -8. Sedimentation rates between ^{14}C dates and mf-7 (dated to 1830) are 0.19 cm year^{-1} in core II.1 and 0.18 cm year^{-1} in core III.2. These rates are similar to those reported by Wright et al. (1998) for a 16 m long core collected mid-channel between transects II and III (0.15 cm year^{-1}).

Cesium-137 dating

Activity profiles for ^{137}Cs show well-defined peaks in all 20 analyzed cores corresponding to the 1964 maximum in atmospheric deposition from nuclear testing (Fig. 5). Preliminary counts on several of the detailed cores indicated that the ^{137}Cs peak was closely aligned with mf-2, and only a few counts centered around mf-2 were needed to define the ^{137}Cs maximum in subsequent analysis of the top/bottom cores. The core depth of the ^{137}Cs marker generally exceeds 1 m in the upper end of the lake (transect I), which is equivalent to a mean sedimentation rate of more than 3 cm year^{-1} over the last three decades. The sediment column overlying the ^{137}Cs peak tends to decrease down river, although there is considerable variation within each transect. In transect V at the lower end of the lake the 1964 ^{137}Cs marker occurs between 0.4 and 0.5 m, which still represents an annual sedimentation rate in excess of 1 cm. These high rates of burial and the high silt/clay content of Pepin sediments tend to limit diffusion (or mixing) of sedimentary ^{137}Cs and create near-ideal conditions for preservation of sharply defined ^{137}Cs peaks (Van Metre et al. 1997).

Lead-210 dating

Total ^{210}Pb activity shows a roughly monotonic decline with sediment depth in the upper strata of cores from mid- and lower-lake transects (III–V), while activity profiles in the upper lake transects (I and II) are more irregular and exhibit numerous kinks and flat spots (Fig. 6). Surface activities are quite low, especially in upper lake cores, and range from 5.7 pCi g^{-1} in core V.1 to 2.0 pCi g^{-1} in core I.2. Background (supported) ^{210}Pb is well defined at depth in all cores by numerous strata with near constant activity. Supported ^{210}Pb values are lowest in cores from the upper end of the lake (0.9 pCi g^{-1} in transect I) and increase down lake (1.5 pCi g^{-1} in transect V). However, the two dated

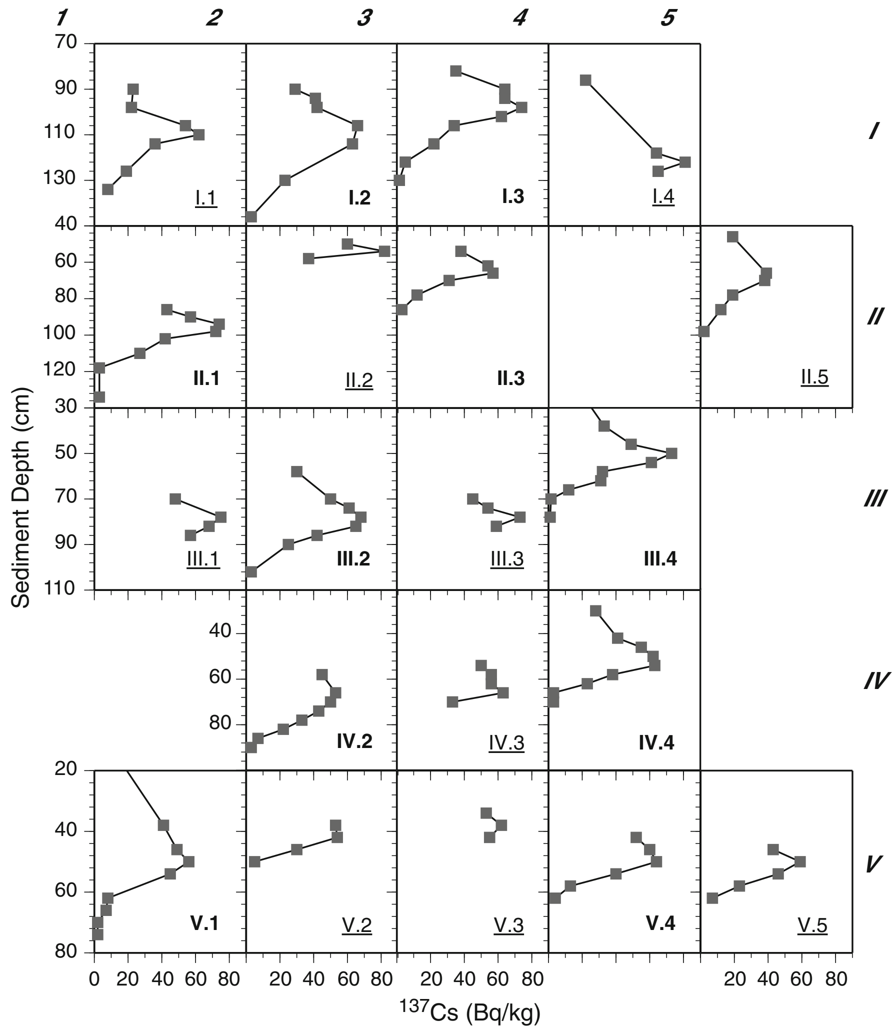


Fig. 5 Cesium-137 profiles for detailed (*bold*) and top/bottom (*underlined*) cores. Maxima represent 1964 time horizon

cores from each transect show virtually the same supported ^{210}Pb, providing evidence that supported activities are reasonably constant for any given reach of the lake. The maximum sediment depth at which unsupported ^{210}Pb is found is greatest in upper lake cores (>2 m in transect I) and shallowest in lower-lake cores (1 m in transect V), which is consistent with the down-lake decrease in sedimentation rates indicated by other stratigraphic analyses (magnetic susceptibility, pollen, ^{137}Cs).

The average lake-wide flux of ^{210}Pb to Lake Pepin is 2.3 pCi cm^{-2} year^{-1}, or about 5 times the mean atmospheric deposition rate for the region (0.45 pCi cm^{-2} year^{-1}) (Urban et al. 1990). Although a large portion of the ^{210}Pb load to Lake Pepin is clearly delivered by the Mississippi River, the annual lake-wide accumulation (1.7 Ci) represents <1% of the ^{210}Pb falling on the watershed—assuming an in-lake retention of 75%, similar to particulate matter (James et al. 1998). It appears that most atmospheric ^{210}Pb is retained in the watershed, and what little does make it to Lake Pepin can be largely attributed to direct atmospheric deposition to the surface of the Mississippi River and its tributaries (although some portion of the ^{210}Pb is certainly delivered by soil erosion).

All activity profiles show flat spots and other changes in slope that represent historic changes in sediment flux to the core sites (Fig. 6). Such data are best interpreted using the c.r.s. model, which assumes a constant flux of ^{210}Pb to the core sites but allows sediment accumulation to vary. The assumption of a constant ^{210}Pb input is generally valid for lakes that

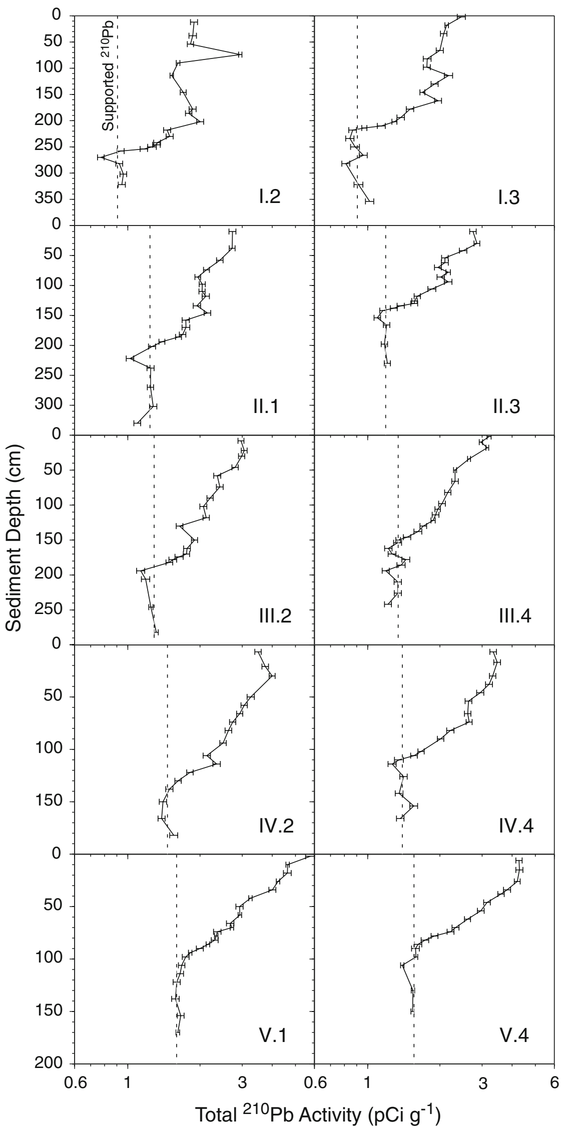


Fig. 6 Total ^{210}Pb activity plots for 10 detailed cores. Supported ^{210}Pb indicated by *dashed line*; *error bars* represent ±1 SD

obtain most of their ^{210}Pb by direct atmospheric deposition. However, Lake Pepin probably receives a substantial flux of ^{210}Pb as part of the sediment load from the Mississippi River, and the input to individual core sites may have varied over time with changes in river flow or human alterations of its very large catchment. Lead-210 dating of these cores is also uncertain because of the very low values for unsupported ^{210}Pb (calculated as the difference between total and supported ^{210}Pb). Unsupported activities are particularly low in Pepin sediments, because high sediment fluxes, especially in the upper lake, severely dilute the ^{210}Pb inputs. Although the ^{210}Pb profiles from Lake Pepin can be interpreted using the c.r.s. model, the resulting dates must be compared with independent dating markers to ascertain their reliability.

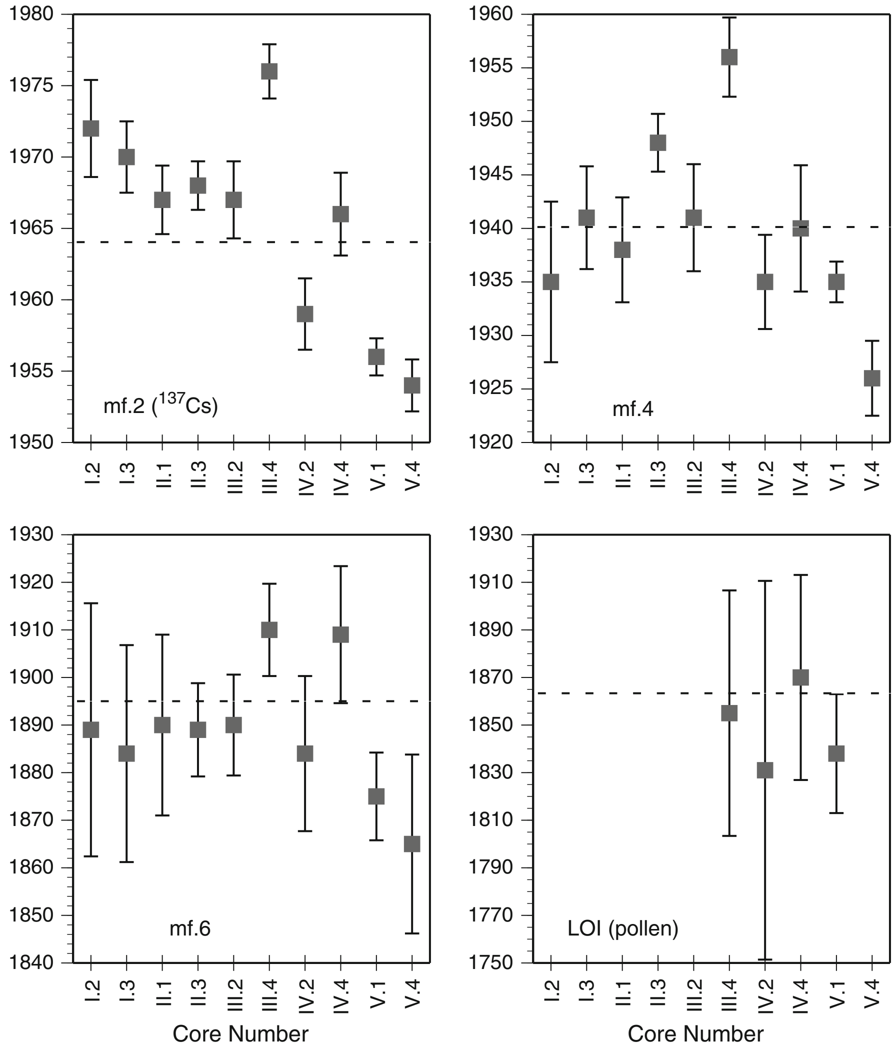
Cesium-137 and pollen analysis (together with LOI) provide two dating markers with which the ^{210}Pb results may be compared: the 1964 ^{137}Cs peak and the 1860 *Ambrosia* rise. In addition, two peaks in magnetic susceptibility (mf-4 and -6) are readily identified in all cores and can be used to compare the synchronicity of ^{210}Pb dates at depths intermediate between the ^{137}Cs and pollen markers. This comparison clearly shows that most ^{210}Pb chronologies deviate substantially from one another and from the known dates (Fig. 7). Lead-210 dates at the depth of the ^{137}Cs peak are either significantly older or younger than 1964. There is an equally large scatter about the magnetic markers, with mf-4 centered at 1940 and mf-6 around 1890. Lead-210 chronologies from only four cores extend to 1860, and the dates at this maker have very large uncertainty (25–70 years).

The most likely explanation for the discrepancies among core chronologies is a changing flux of ^{210}Pb to individual core sites. A number of post-settlement changes to Lake Pepin, including increased sediment loads, changes in flow regime, basin infilling, and delta progradation, could have altered the pattern of sediment deposition and ^{210}Pb accumulation within the basin. The c.r.s. model can be modified to accommodate changes in core-specific ^{210}Pb flux by integrating ^{210}Pb inventories from time-synchronous units of a representative set of cores (Oldfield and Appleby 1984). The primary assumption here is one of constant ^{210}Pb input to the entire lake basin rather than to individual core-sites. In the case of Lake Pepin, magnetic susceptibility features mf-2 (the ^{137}Cs peak), -4, -6, and the *Ambrosia* rise (or LOI equivalent) provide the depth markers for synchronizing the 10 analyzed cores. In this basin-wide c.r.s. model, $B(\xi)$ is the total unsupported ^{210}Pb beneath the entire sediment layer defined by depth marker ξ, and the age t of marker ξ is given by:

$$B(\xi) = B(o) \cdot e^{-kt} \tag{1}$$

where k is the decay constant for ^{210}Pb (0.03114 year^{-1}). $B(\xi)$ and $B(o)$ are calculated by summing the corresponding ^{210}Pb inventories for

Fig. 7 Uncorrected ^{210}Pb dates calculated by the c.r.s. model for individual cores, showing deviations from synchronous stratigraphic markers. Only four cores had dates extending to the 1860 pollen (LOI) marker; *error bars* represent ±1 SD



individual cores weighted by the portion of the depositional basin each core represents.

The basin-wide c.r.s. model yields the following dates for Lake Pepin: mf-2 (1967), mf-4 (1940), mf-6 (1890), and the *Ambrosia* rise (1841). The ^{210}Pb date of 1967 on mf-2 is very close to that determined independently by ^{137}Cs (1964), lending support to the basin-wide c.r.s. model. However, the pollen date is clearly too old, indicating that a small amount of unsupported ^{210}Pb is missing from the basin-wide inventory. This missing amount, which probably resulted from the difficulty of estimating near-background values of unsupported ^{210}Pb in the upper lake cores, can be calculated by fitting the lowermost ^{210}Pb date at the *Ambrosia* rise to 1860. The effect of this small addition of unsupported ^{210}Pb on the other dates is negligible except for a slight shift of mf-6 to 1894.

Detailed ^{210}Pb chronologies were established for individual cores by fitting the c.r.s. model to fixed dates at the four stratigraphic markers: mf-2 (1964), mf-4 (1940), mf-6 (1895) and the *Ambrosia* rise (1860). Dates between fixed markers ξ_1 and ξ_2 were determined by calculating the unsupported ^{210}Pb inventory below the lower of the two markers $A(\xi_2)$ as:

$$A(\xi_2) = \frac{A(i)}{(e^{k\cdot\Delta t} - 1)} \tag{2}$$

where $A(i)$ is the ^{210}Pb inventory for the interval between ξ_1 and ξ_2, and Δt is the time between the two fixed dates. The ^{210}Pb inventory above the upper dating marker $A(\xi_1)$ of age t was calculated as:

$$A(\xi_1) = [A(i) + A(\xi_2)] \cdot (e^{kt} - 1) \tag{3}$$

and the age at core depth x between ξ_1 and ξ_2 is given by:

$$A(x) + A(\xi_2) = [A(\xi_1) + A(i) + A(\xi_2)] \cdot e^{-kt} \tag{4}$$

where $A(x)$ is the ^{210}Pb inventory between x and ξ_2. The effect of these calculations is to adjust the ^{210}Pb inventory for a core at each dated marker under the assumption that the ^{210}Pb flux to the core site has remained relatively constant during the interval between markers. Although it is more likely that the ^{210}Pb flux varied continuously over time, the resulting dates are closely constrained by the fixed markers and are unlikely to be far from true.

Sediment accumulation rates

A composite chronology for each detailed sediment core was compiled from fitted ^{210}Pb dates (1860 to present) and ^{14}C-dated magnetic features for pre-settlement strata. A date of 1830 was ascribed mf-7 (the settlement horizon), and ^{14}C dates of 1473 AD and 1284 AD were fixed on mf-7.5 and -8, respectively. Sediment flux was calculated as the cumulative dry mass between dated strata divided by the time elapsed. For top/bottom cores a single "modern" sedimentation rate representing the last 35 years was calculated from the ^{137}Cs marker, while pre-settlement sediment accumulation was estimated from the dated magnetic features (as in the detailed cores). The pre-settlement sedimentation rate from core IV.4 was applied to two adjacent cores, IV.2 and IV.3, that truncated above mf-7.5; the three cores exhibit parallel susceptibility profiles which suggests similar sedimentation rates in pre-settlement times.

All detailed cores show a dramatic increase in sediment accumulation over the course of the last 200 years (Fig. 8). Accumulation rates double around the time of European settlement, increase gradually during the first few decades of the twentieth century, and then rise sharply between 1940 and 1960. Most of the cores show a clear decline in sediment flux during the 1970s followed by a return to peak values during the last two decades. These trends are broadly synchronous among cores although differing in detail from site to site.

Sediment accumulation rates are highest in cores from the upper end of the lake and decrease

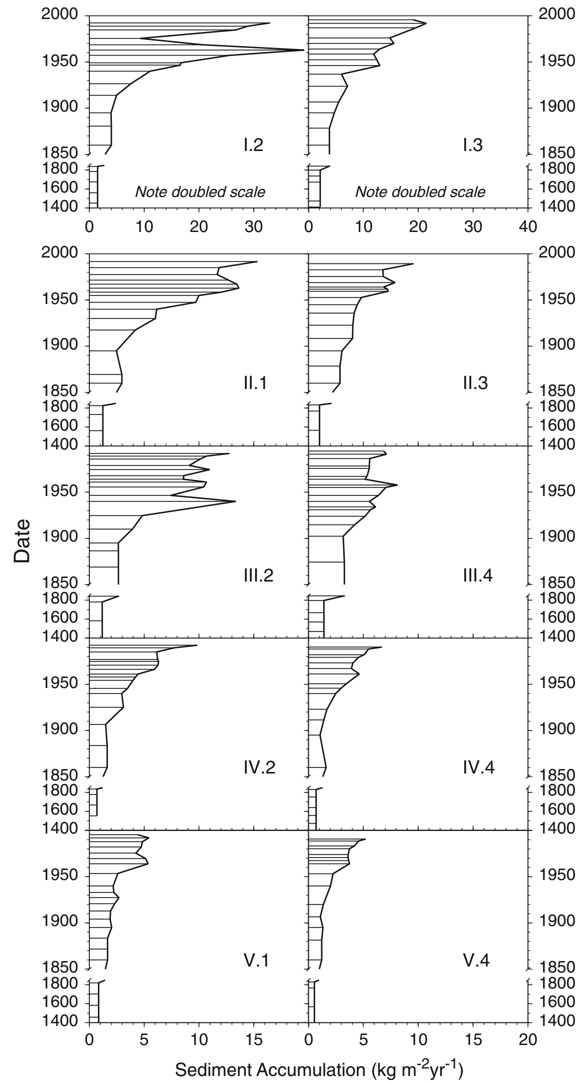


Fig. 8 Sediment accumulation rates versus sediment age for 10 detailed cores

progressively down stream. Pre-settlement accumulation rates in cores from transect I range from 1.3 to 2.1 kg m^{-2} year^{-1}, while those from transect V vary from 0.5 to 0.8 kg m^{-2} year^{-1} (Fig. 8). Modern sedimentation rates are about an order of magnitude higher than pre-settlement rates throughout most of the basin (ranging from 7–15 kg m^{-2} year^{-1} in transect II to 3–5 kg m^{-2} year^{-1} in transect V), except in uppermost transect I where present-day rates (20–30 kg m^{-2} year^{-1}) average about 15 times pre-settlement rates. The larger rate increase in cores from transect-I may represent enhanced sedimentation caused by progradation of the Mississippi delta at the upper end of the lake. Higher rates of sediment infilling in the upper reaches of Lake Pepin have been noted by a number of previous investigators (Maurer et al. 1995; McHenry et al. 1980; Rada et al. 1990).

Sediment-phosphorus content

Total sediment-P (TP_{sed}) concentrations are relatively uniform across the depositional basin of Lake Pepin. Pre-settlement values range from 0.6 to 0.8 mg g^{-1} dry sediment, with lower lake cores (transects IV and V) just slightly higher than mid- and upper lake cores (Fig. 9). Total-P_{sed} shows little variation during pre-settlement times but increases markedly after about 1850, reaching peak values of 1.6–1.8 mg g^{-1} between 1950 and 1970. Many of the cores exhibit an earlier peak of 1.0–1.4 mg g^{-1} between 1890 and 1910, followed by a local minimum around 1920–1930. Total-P_{sed} concentrations decline noticeably after 1970 in upper- and mid-lake cores (transects I–III).

Roughly half of the P in Lake Pepin sediments is composed of NaOH-extractable P (NaOH-P), with HCl-extractable P (HCl-P) and residual P (organic-P) each making up about one-fourth (Fig. 9). NH_4Cl-P averaged <5% of TP_{sed} in all cores and is summed here with NaOH-P. These proportions vary spatially within the basin as well as stratigraphically within cores. NaOH-P comprises 30–45% of the total in pre-settlement strata, increases to 60–70% during peak P concentrations in the 1960s and 1970s, and declines toward pre-settlement proportions after 1970. The percentage of HCl-P drops to around 10–15% following settlement, while organic-P shows a variable pattern, rising in some cores (IV.2, III.4, II.1) but not others (V.1, V.4). HCl-P trends toward pre-settlement proportions after 1970 in cores from the upper-lake transects (I and II).

Overall, TP_{sed} concentrations in recent decades are roughly twice those of pre-settlement times, and much of the increase can be ascribed to labile forms of inorganic-P (NaOH-P). The recent (post 1970) drop in P content of upper and mid-lake cores corresponds to the increase in carbonate content noted earlier. As sedimentation rates also rebound during this time period, it seems likely that P concentrations drop because of dilution from inputs of P-poor sediments.

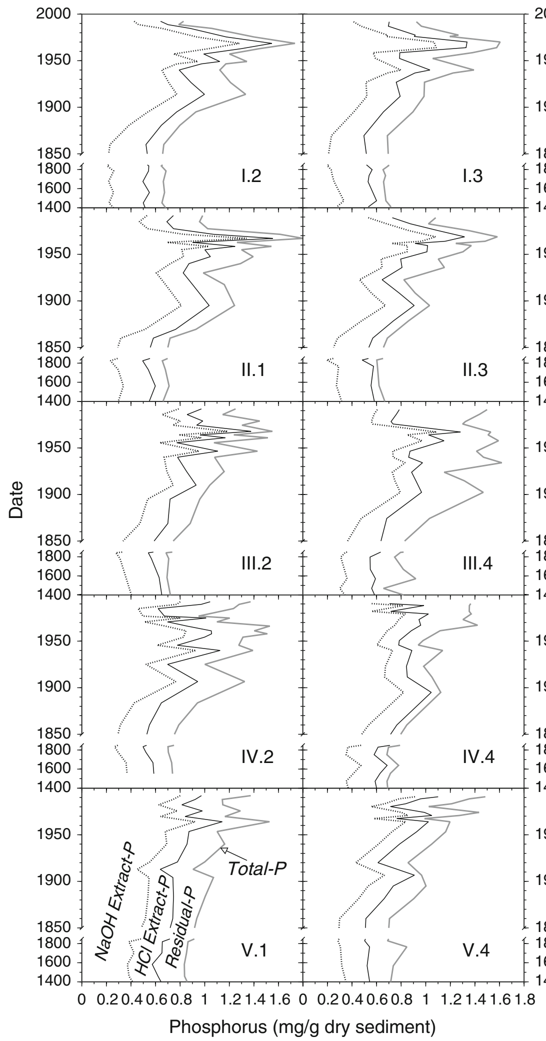


Fig. 9 Concentrations for total phosphorus and P fractions versus sediment age for 10 detailed cores. *Plots* are stacked; total is sum of NaOH-P, HCl-P, and residual-P

Diatom stratigraphy and inferred lakewater-TP

A total of 145 taxonomic entities were identified in the 10 stratigraphic samples analyzed for fossil diatoms. Sample intervals were 4-cm thick and integrated from 2 to 12 years of accumulation. Samples older than 1920 were very low in diatoms with the lowest concentrations occurring around 1900. Diatom microfossils were slightly more numerous and most heavily silicified in the bottom sample (c. 1760). Preservation of the more lightly silicified taxa did not appear to be a problem, as intact valves of *Asterionella formosa* were present to a core depth of 92–96 cm (an uncounted level dating to c. 1880). The good preservation found in core V.1 stands in contrast to that reported previously by Ohl (1992) for a 1989 core from lower Lake Pepin. Ohl found numerous diatom fragments and low abundance at depth in his profile, which he attributed to poor preservation. Most of the diatoms found in core V.1 are characteristic of lentic environments and are thought to derive principally from in-lake production.

A total of 30 taxa from the Lake Pepin data were used for lake-water TP reconstruction after matching species with published optima from the Bennion (1994) calibration set; these taxa represented 55–73.5% of the total diatoms in each sample. After addition of species optima from Reavie et al. (1995), the number of taxa used in the reconstruction rose to 36 and represented 77–90% of the total diatom abundance (Fig. 10). In particular, *Aulacoseira subarctica* (O. Müller) Haworth, is not present in the Bennion data set, but is included in those of Reavie et al. (1995). It is an important taxon from 1900 to 1940 and constitutes 13–27% of the total diatom assemblage in these samples.

Two different TP reconstructions were produced from the Pepin diatom data. The first (TP-1) used additional species optima from Reavie et al. (1995) only for those taxa absent from the Bennion data set. The second TP inference (TP-2) was constructed using optima from Reavie et al. for all *Aulacoseira* and *Fragilaria* species (Fig. 10). These taxa are infrequent among the high-TP lakes sampled by Bennion, but are well represented at the lower TP range of the Reavie et al. data set. Because these taxa are also dominant in the deeper strata of the Pepin core, the second TP inference (TP-2) is probably a more accurate reconstruction of pre-settlement nutrient conditions than TP-1. TP values from this second inference model are applied to pre-1860 strata in the following discussion and are used for reconstructing a P mass-balance for the lake.

Benthic diatom species have their highest abundance in the two pre-settlement samples (Fig. 10). At 1860, benthic and planktonic species each compose 50% of the diatom assemblage. Planktonic diatoms continue to increase above this level and constitute $\geq$90% of the assemblage from 1940 to the present. Chrysophyte cysts comprise ca. 10% of the microfossil assemblage in the lower samples, reaching a maximum of 16% around 1900. Their abundance declines rapidly after 1920.

The high percentage of benthic diatom species and chrysophyte cysts in the lower samples of the core indicate that prior to European settlement, clear water conditions existed for at least part of the year in Lake Pepin. Mean TP values are lowest in these samples (50–55 μg l^{-1}; TP-2). However, there are several lines of evidence that suggest these reconstructed values may be too high for pre-settlement Lake Pepin. First, diatom reconstructions for 55 Minnesota Lakes show a much lower pre-settlement TP than that

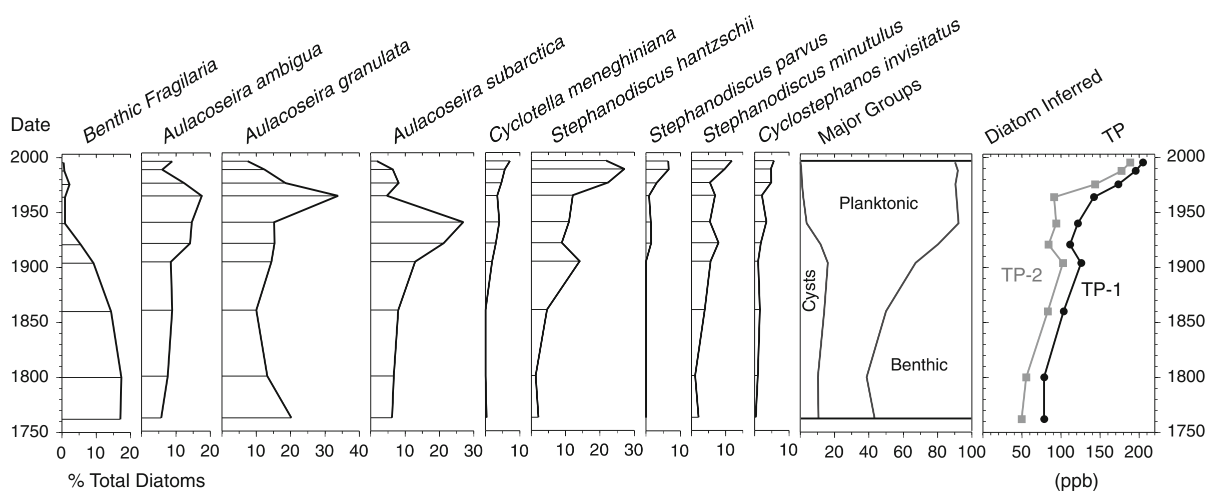


Fig. 10 Diatom concentration diagram from core V.1 showing selected taxa and total-phosphorus reconstructions by weighted-averaging regression and calibration; TP-1 and TP-2 represent alternative reconstructions based on species optima from different data-sets

derived for Lake Pepin: 23 ± 13 μg l^{-1} (mean ± 1 SD), with only five lakes in the data set exceeding 40 μg l^{-1} (Ramstack et al. 2004). TP reconstructions for the nearby St Croix River, a tributary to Lake Pepin, are also on the order of 30 μg l^{-1} in pre-settlement times (Edlund et al. this issue). Second, these lower TP values are more similar to natural background concentrations estimated for the UMR from ecoregion models based on minimally impacted USGS reference basins (Smith et al. 2003). And third, a lower pre-settlement TP (35–40 μg l^{-1}) would fit better the P mass-balance reconstructed for Lake Pepin (see below).

Reconstructed mean TP concentrations increase to ca. 80 μg l^{-1} (TP-2) by 1860 and reflect the influence of European settlement and land clearance in the basin. Diatom microfossil concentrations are low in samples just prior to and immediately after this level. The low abundance indicates probable dilution caused by higher sediment loads. A peak in inferred TP occurs around the turn of the century (125 μg l^{-1}) and corresponds with the first increases in *Stephanodiscus* species and the beginning rise in *Aulacoseira* abundance. These diatom groups have high and medium-high P optima, respectively. *Cyclotella meneghiniana* also occurs at this level and increases to the surface of the core. This taxon has been reported from nearshore areas in nutrient-enriched Lakes Erie and Ontario (Stoermer 1978), and its rise in Lake Pepin is consistent with an increase in nutrient loading.

The onset of European settlement and the rise in mean TP concentrations corresponds with increased abundance of planktonic taxa in the core (Fig. 10). Although a common signal for cultural eutrophication, the relative increase in planktonic diatoms does not result from competitive suppression of the benthic community. Rather, both benthic and planktonic diatoms respond to cultural eutrophication, and overall diatom productivity increases by more than 15× from pre-settlement to the present (Triplett 2008). A similar increase in benthic production is reported in this issue for nearby Lake St Croix (Edlund et al. this issue) as well as for other lakes with well-constrained whole-basin diatom records (e.g. Anderson 1989).

A decline in inferred-TP around 1920 (110 μg l^{-1}) corresponds with a local minimum in sedimentary P concentrations and may indicate reduced nutrient loading resulting from a temporary cessation of watershed disturbance and possibly from reduced flows in the Mississippi during the dust-bowl era. The rise in mean TP after 1965 (from 140 to 170 μg l^{-1}) signals another major perturbation in the river. Diatom assemblages shift from an *Aulacoseira* (medium–high optima) dominated system to a *Stephanodiscus* (high optima) dominated one. The rise in *Stephanodiscus* species indicates increased nutrient loading to the lake. Additionally, *Actinocyclus normanii* f *subsalsa* first occurs at the 1940 level. It is a taxon common in highly polluted nearshore regions and bays in the Great Lakes and is indicative of areas with high industrial activity (Stoermer 1978).

Mean TP concentrations increase continuously from 1975 to the present (from ~170 to 200 μg l^{-1}). No apparent decrease in TP concentrations occurs at the surface, indicating that nutrient levels have continued to rise. However, historical data on summer TP concentrations in Lake Pepin (1976–1991) do not show a systematic increase, but fluctuate about a mean of 240 μg l^{-1} (Heiskary and Vavricka 1993); a mean of 180 μg l^{-1} was recorded in 1964–1965 (FWPCA 1996). This discrepancy with diatom-inferred TP may simply reflect the coarse temporal resolution of the diatom data, or may indicate that the diatoms are responding to other factors (e.g. light limitation caused by suspended sediment) in addition to mean summer P concentrations.

Discussion

Whole-lake fluxes

Fluxes for each sediment fraction were calculated for individual core sites as the product of the sediment accumulation rate and the concentration of the fraction in different strata. In turn, lake-wide fluxes were determined by weighting the flux of each core by the portion of the depositional basin it represents (see "Methods"). In this study we calculated whole-lake fluxes at decadal intervals from the present to 1930, at 20-year intervals from 1930 to 1890 and 30-year intervals from 1890–1830; a single average flux was determined for all analyzed strata older than 1830 (Fig. 11). Fluxes were harmonized in this manner because the dating intervals obtained by ^{210}Pb were different for each core; the averaged

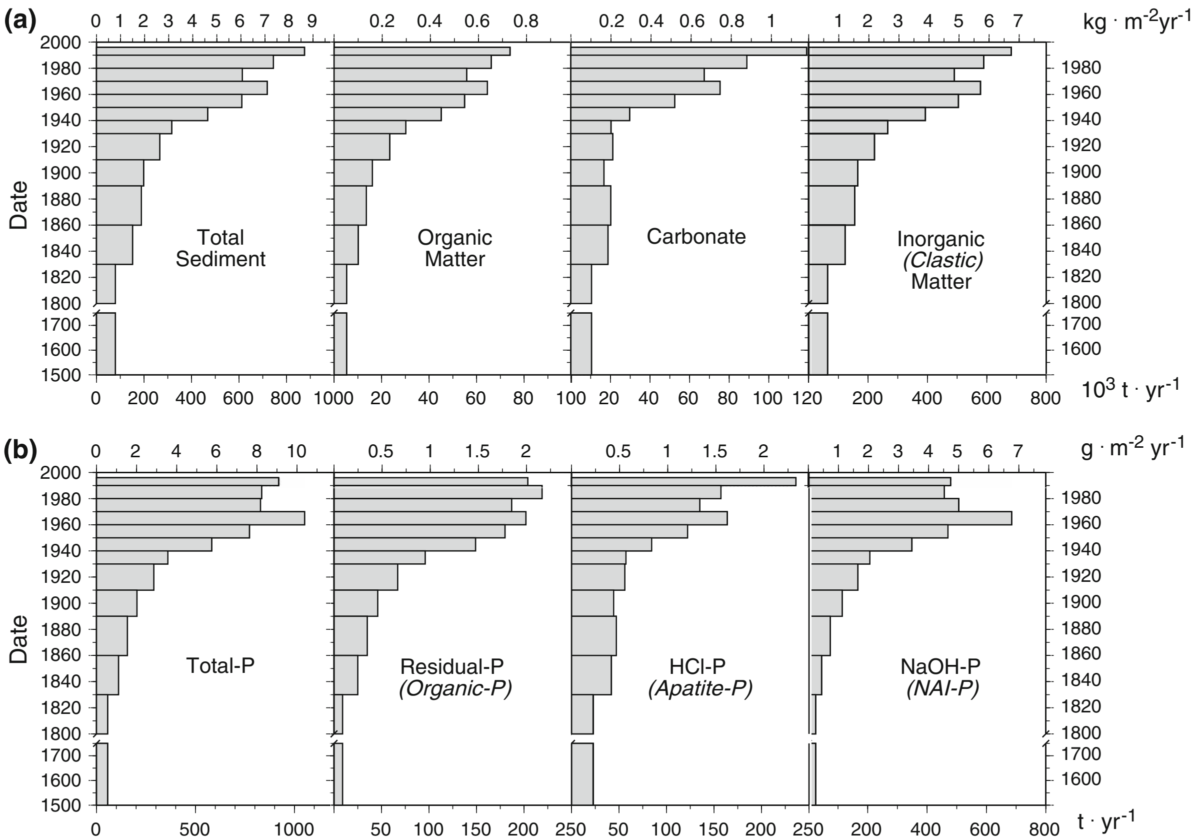


Fig. 11 Annual whole-basin sediment (**a**) and phosphorus (**b**) accumulation in Lake Pepin

intervals are consistent with the temporal resolution of geochemical analysis and core dating.

Annual sediment accumulation in Lake Pepin has increased by more than an order of magnitude, from 79,000 t during pre-settlement times to 876,000 t in the 1990s (Fig. 11). The accumulation increase is relatively gradual during the first century following settlement, but accelerates markedly during the 1940s and 1950s. Sediment flux appears to plateau at about 700,000 t year^{-1} after 1960, with a modest drop during the 1970s and a small peak in the 1990s. The present-day rate is very close to mass-balance estimates of sedimentation (680,000 t year^{-1}) based on inflow/outflow measurements for 1994–1996 (James et al. 1998). Moreover, the sediment core results for 1990–1996 integrate high flow years (e.g. 1993) and hence should be expected to be somewhat higher than 1994–1996. The convergence of these two estimates of modern mass flux lends considerable weight to historical estimates of sediment accumulation from our retrospective study.

Fluxes of the major sedimentary components—organic matter, carbonates, and inorganic matter (clastics)—parallel the historic changes in total sediment accumulation (Fig. 11). Organic matter increases from a pre-settlement flux of 5,000 t year^{-1} to a modern rate of 74,000 t year^{-1}, while clastic inputs increase from 64,000 to 682,000 t year^{-1}. Carbonates show a slightly different pattern, holding relatively constant at about 20,000 t year^{-1} from settlement to 1940 and then rising dramatically thereafter to peak rates of 119,000 t year^{-1} in the 1990s. The rapid increase in carbonate flux since 1940 may reflect increased algal productivity in Lake Pepin, which could drive calcite precipitation though greater uptake of CO_2 (Engstrom and Swain 1986; Hodell et al. 1998). The carbonate flux closely tracks whole-lake P trends and diatom-inferred TP for the water column, suggesting that the most dramatic trophic changes in Lake Pepin have occurred since c. 1945.

The lake-wide flux of TP_{sed} mirrors the historic increase in total sediment accumulation (Fig. 11).

Modern rates (800–900 t $year^{-1}$) are about 15 times pre-settlement rates (60 t $year^{-1}$) and are relatively constant following a 1960s peak of 1000 t $year^{-1}$. All of the various P fractions show the same broad post-settlement increase, although differing somewhat in detail. NaOH-P, the largest fraction, exhibits the greatest change, rising to a peak flux of 680 t $year^{-1}$ during the 1960s and declining to present-day rates of 480 t $year^{-1}$; the 1960s flux is more than 25 times the pre-settlement accumulation rate (25 t $year^{-1}$). The flux profile for HCl-P is very similar to that for carbonate, holding steady at 40–50 t $year^{-1}$ from 1830 to 1940 and then rising sharply to 160 t $year^{-1}$ during the next two decades; the 1990s carbonate peak also shows up in HCl-P accumulation. The distinctive features of the HCl-P profile and their correspondence with carbonate flux are a clear indication that the HCl-P fraction is closely bound to sedimentary carbonates. The annual flux of residual (organic) P increases about 20 times from pre-settlement (10 t) to present-day values (200 t); fluxes have been relatively constant since about 1950.

Our estimate of present-day sedimentation rates for TP_{sed} (920 t $year^{-1}$) is somewhat higher than mass-balance calculations would indicate. Annual retention of P in Lake Pepin sediments averaged 510 t from 1994 to 1996 based on the difference between TP inflow (3,930 t $year^{-1}$) and outflow (3,420 t $year^{-1}$) (James et al. 1998). However, these monitoring data do not include the 1993 flood year in which exceptional sediment loading almost certainly raised the average TP_{sed} flux to the stratigraphic record for 1990–1996. Moreover, the mean in-lake retention estimated by James et al. (1998) is only 13% of annual inputs, meaning that small uncertainties in estimating inflows or outflows could also explain some of the difference between their estimate of P accumulation and ours. These differences notwithstanding, the convergence of two totally independent estimates of modern P sedimentation provides compelling evidence that the stratigraphic record offers a reliable measure of historical P loading to the UMR.

Phosphorus mass-balance

Because of its relatively short residence time (6–47 days), Lake Pepin retains in its sediments a relatively small portion of the TP load from the Mississippi River. Current estimates from inflow/outflow measurements for 1994–1996 place in-lake retention at about 13%, with the remaining 87% lost though outflow (James et al. 1998). If we assume that P retention has remained relatively constant over time, then historical P loading—estimated by dividing annual P accumulation in Lake Pepin sediments by 13%—has increased progressively from 430 t $year^{-1}$ in pre-settlement times to 7,000 t $year^{-1}$ at the present day. However, these estimates are likely to be in error, because relatively small changes in retention could have a large effect on the rate of P sedimentation. Change in discharge (which would affect residence time), eutrophication and associated changes in lake-bottom redox conditions (which could enhance P-release from sediments), and increased sedimentation rates (which might have the opposite effect and enhance P burial) have occurred since European settlement and have likely altered P retention in Lake Pepin.

A preferable alternative would be to estimate historical losses of P from Lake Pepin through Mississippi River outflow and calculate P loading to the lake as the sum of sedimentation and outflow. Outflow losses can be calculated from historical flow records and reconstructions of water-column P concentrations from fossil diatoms in Pepin sediments. Such methods, applied by Rippey and Anderson (1996) to a small eutrophic lake in Northern Ireland, show reduced P sedimentation during periods of increased lake-water TP, illustrating that assumptions of constant P-retention can be highly misleading.

Discharge records for the Mississippi River at the USGS gauging station at Prescott, WI (below the confluence with the St Croix River) extend back to 1928. Earlier flows at Prescott can be estimated from those at St Paul, MN (back to 1892) and St Croix Falls, WI (back to 1910 and intermittently to 1902) by scaling the discharge at those upstream stations to flows at Prescott for the period of common record (1928–1996). This composite record (Fig. 12) shows large variations in mean annual flow, with persistently low values during the 1920s and 1930s and substantially higher flows from the 1940s onward, especially during the last three decades. Flows prior to 1892 must be extrapolated from the period of record; our best estimate is the average discharge from 1892 to 1930, which excludes the extreme low flows of the Dustbowl era and high flows of the late

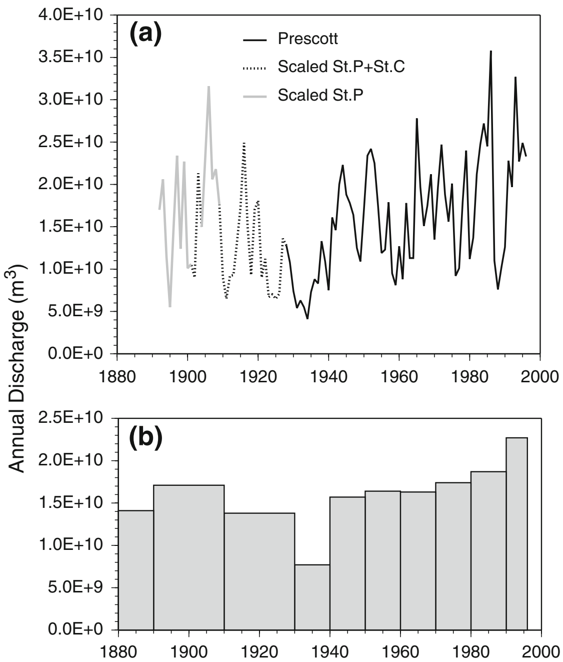


Fig. 12 Annual discharge of the Mississippi River at the USGS gauging station at Prescott, Wisconsin (**a**); *solid line* indicates period of actual measurement; *dashed* and *shaded lines* represent inferred flows scaled from older records of the Mississippi River at St Paul, Minnesota (St P) and the St Croix River at St Croix Falls, Wisconsin (St C). Mean decadal discharge (**b**) of the Mississippi River at Prescott

twentieth century that resulted, in part, from hydrological alterations and land-use changes (wetland destruction, ditching, and subsurface drainage).

Reconstructed P outflow from Lake Pepin, calculated at decadal intervals as the product of diatom-inferred TP and mean discharge, shows a gradual rise from 700 t year^{-1} in pre-settlement times to 2,200 t year^{-1} around the turn of the century (Fig. 13). Phosphorus outflow drops sharply during the low-flow decades of the 1920s and 1930s, returns to 1,900–2,300 t year^{-1} between 1940 and 1970, and then rises sharply to present-day values of 4,500 t year^{-1}. Our estimate for the 1990s compares well with direct measurement of P outflow (3,400 t year^{-1}) for 1994–1996 (James et al. 1998).

Historical P loading to Lake Pepin from the Mississippi River, the sum of P outflow and P sedimentation, increases by a factor of three from 1830 (800 t year^{-1}) to 1900 (2,400 t year^{-1}), declines during the 1920s and 1930s to a minimum of ca. 1,200 t year^{-1}, and then rises continuously from the 1940s (2,500 t year^{-1}) to the present decade (5,450 t year^{-1}) (Fig. 13). Again, our 1990s estimate for P loading (which includes the 1993 flood year) is only slightly higher than P inflow measurements by James et al. (1998) for 1994–1996 (3,900 t year^{-1}).

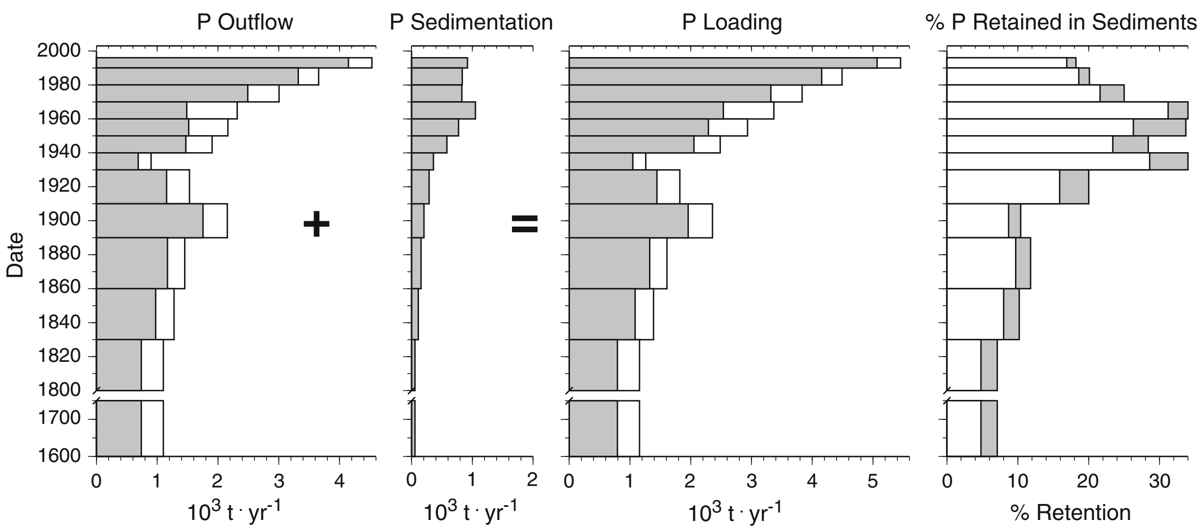


Fig. 13 Reconstructed phosphorus mass-balance for Lake Pepin. Phosphorus loading is calculated as the sum of P outflow and P sedimentation. Two estimates are shown based on diatom inference models TP-1 (*open bars*) and TP-2 (*shaded bars*). TP-2 estimates are considered to be more accurate at low phosphorus levels and are applied to pre-1860 strata in the discussion section; TP-1 estimates are used for 1860 to present

According to our reconstructions, P loading to Lake Pepin has increased about sevenfold from 1830 to the present. Changes in discharge account for some of the trend, and certainly explain much of the decade-to-decade variation, but the overall increase is driven by rising P concentrations in the water, and ultimately anthropogenic impacts in the watershed (Mulla and Sekely this issue).

These mass-balance calculations show that in-lake retention of P has not remained constant over time, but has risen markedly since the turn of the century (Fig. 13). Prior to European settlement, only 7% of the P inflow was sedimented in Lake Pepin; this value increased to 10% after 1830 and then remained steady until about 1910 when it rose to 16%. Phosphorus retention peaked at 23–32% between 1930 and 1970 and then declined progressively to present-day values of 17%. Some of this change appears to be driven by discharge, particularly the high retention rates of the 1930s (30%) and the recent decline of the last three decades. Longer residence times during low flows (e.g. 1930s) should favor higher retention rates, and conversely rapid flushing during high flows (1970s–1990s) should retard P sedimentation. However, differences in flow alone cannot explain the overall increase in P retention in the twentieth century, and other factors favoring P sedimentation must be invoked. The most likely explanation is the large increase in sediment accumulation that begins in the early 1900s. Increasing sedimentation rates should enhance P retention either through a higher particle flux (scavenging P from the water column) or more rapid burial (slowing diffusive or advective release of sedimentary P). Eutrophication, which often leads to greater P release through hypolimnetic anoxia (Marsden 1989), appears not to have affected P retention to nearly the same degree as sediment burial rates or river flows. Although experimental studies show much higher rates of P-release from Pepin sediments under anoxic conditions (MWCC 1993c), the water column of Lake Pepin is usually oxygenated year-round (Heiskary and Vavricka 1993), and bottom-water anoxia is restricted to low-flow conditions.

The low P retention rates (7%) in pre-settlement times also require further examination. P retention rises to 10% immediately following European settlement in 1830, which is curious in that there are few changes at this time that might account for higher P burial—as compared to the rest of the nineteenth century when P retention remains steady. Rather, it seems more likely that 7% P retention is an underestimate that results from an error in the mass balance—specifically an overestimation of lake-water TP based on diatom reconstruction. If pre-settlement TP values were 35–40 μg l^{-1}, rather than the 50 μg l^{-1} from the diatom model (TP-2), in-lake P retention would be 9–10%, and there would be no step increase following settlement in 1830. Conversely, a higher estimate for lake-water TP in pre-settlement times (assuming 50 μg l^{-1} was too low), would lower in-lake P retention and further accentuate the step increase at settlement.

Lake infilling

Sediment from the Mississippi River has been filling Lake Pepin since the lake was formed 10,000 ^{14}C years ago. The lake is thought to have originally extended upstream as far as St Paul according to bridge-boring records (Zumberge 1952), and a 16-m core of lacustrine sediment recovered mid-lake by Wright et al. (1998) indicates a once much deeper basin. However, the rate of infilling has clearly accelerated in the 170 years since European settlement, greatly shortening the projected life of the lake. Volumetric sediment accumulation, calculated by dividing the dry-mass sedimentation rate by the mean bulk density for each core, indicates that lake-wide infilling has increased from 150,000 m^3 $year^{-1}$ in pre-settlement times to more than 1,600,000 m^3 $year^{-1}$ (about 1.6 cm $year^{-1}$ over the entire basin) during the 1990s (Fig. 14). This calculation corrects for compaction and de-watering that occurs as sediments are buried by subsequent deposition.

Extrapolating present-day accumulation rates into the future, the remaining volume of Lake Pepin (553×10^6 m^3 in 1990) will be filled completely in about 340 years. And given its much higher accumulation rates (3.0 cm $year^{-1}$), the shallow upper one-third of the lake (regions I and II, Fig. 1) will cease to be useful for recreation or commerce within about a century. It may take somewhat longer than projected to fill the last remnants of the lake, as sediment trapping efficiency will likely decline with loss of volume (Brune 1953). This obliteration of Lake Pepin will occur in less than one-tenth the time required under pre-settlement conditions.

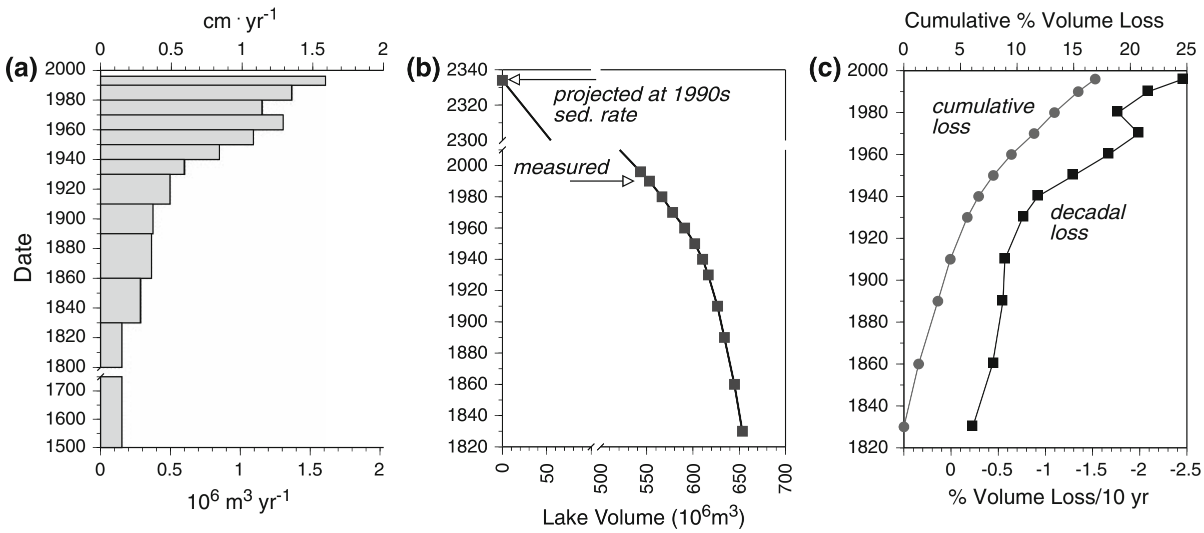


Fig. 14 Linear and volumetric sedimentation rates for Lake Pepin (**a**), projected lake volume from 1990 datum (**b**), and % volume loss relative to 1830 datum (**c**)

Projecting sedimentation rates back in time, lake volume at the onset of European settlement (1830) was 653×10^6 m^3, and by 1890 it was reduced to 634×10^6 m^3 (Fig. 14). Our volume estimate for 1890 is 52×10^6 m^3 smaller than that calculated by Maurer et al. (1995) from 1897 bathymetric maps of the Mississippi River (686×10^6 m^3). This volumetric difference is equivalent to a mean depth of 0.5 m; that is, the average depth of Lake Pepin according to Maurer et al. (1995) was 0.5 m deeper than our sediment cores indicate. This difference is far larger than can be explained by sediment-dating uncertainty, for even if we consider lake volume at the *Ambrosia* rise (1860), the lake was still 41×10^6 m^3 smaller than Maurer et al. (1995) estimate. It seems far more likely that the error lies with early depth surveys of the Mississippi River rather than the explicit measurements of lake infilling that sediment cores provide. This discrepancy may also explain how McHenry et al. (1980) found recent sedimentation rates in Lake Pepin (determined by ^{137}Cs) lower than those in the first half of the twentieth century (as estimated from an 1895 bathymetric survey).

The rate at which Lake Pepin is filling with sediment has increased by more than an order of magnitude since pre-settlement times. Today about 2.5% of the 1830 lake-volume is lost every decade, while just prior to European settlement the decadal loss was 0.23% (Fig. 14). The cumulative change since 1830 has been a decrease of 17%. Under pre-settlement rates the cumulative loss from 1830 to 1996 would have been just 4%, and it would be another 500 years from now before the lake shallowed to its present-day volume.

Conclusions

Historic trends

The sediments of Lake Pepin record an order-of-magnitude increase in the loading of suspended solids from the Mississippi River beginning with European settlement c. 1830 and continuing to the present day. Most of this increase can be traced to the Minnesota River basin, which today contributes over 90% of the sediment to Lake Pepin. Modern fluxes are close to 1 million t annually, and are more than 80% detrital mineral matter. Little of this clastic sediment probably leaves Lake Pepin by outflow, although mass-balance calculations are inconclusive on this matter, as biogenic silica (diatoms) and endogenic carbonates that are produced in the lake are not distinguished from detrital minerals in input/output monitoring. Current estimates of 75% retention of suspended solids (James et al. 1998) provide a minimum estimate of trapping efficiency for clastic materials in the lake.

These sediment loads are currently filling Lake Pepin at an extremely rapid rate. About 17% of the lake volume in 1830 has been replaced by sediment, and if current rates continue, the lake will be filled completely in another 340 years. The upper one-third of the lake, with its higher sediment flux, will be gone in a century. Without this acceleration of sediment loading, Lake Pepin would be on average 1 m deeper today and could persist another 4,000 years.

Sediment P accumulation in Lake Pepin has increased even faster than the total-sediment flux, and current rates of 900 t annually are more than 15 times pre-settlement rates. Part of this rise represents a sevenfold increase in TP loading from the Mississippi River and part reflects more efficient retention of P inflows by bottom sediments. In the 1990s an average of 5,400 t of P entered Lake Pepin annually, and 17% of this load went to the bottom. Retention rates exceeded 20% from 1930 to 1970, while prior to 1910 only 10% of the external P load was retained. More efficient trapping of P in Lake Pepin over the last century probably resulted from higher rates of sediment burial. This observation runs counter to expectations that cultural eutrophication, especially if accompanied by hypolimnetic anoxia, should enhance internal P loading and decrease P-retention (Anderson 1997). However, thermal stratification is weak in Lake Pepin and bottom-waters are seldom if ever anoxic (Heiskary and Vavricka 1993). In situ pore-water gradients indicate P release from Pepin sediments, but at rates similar to those measured in laboratory experiments under oxic conditions (MWCC 1993c). Even if present-day release rates are higher than those in the distant past, they clearly have been overwhelmed by the historic increase in gross P sedimentation.

The historic increase in external P loads has raised TP levels in waters of Lake Pepin at least fourfold (from 50 to 200 μg l^{-1})—and quite possibly more if pre-settlement TP levels were closer to 35–40 μg l^{-1}, as we suspect. Increased nutrient availability is recorded by a marked shift in diatom flora from one dominated by clear-water benthic species and mesotrophic planktonic taxa to exclusively planktonic assemblages characteristic of highly eutrophic conditions.

The most dramatic changes in nutrient and sediment loads to Lake Pepin have occurred since 1940, although gradual increases began shortly following European settlement (c. 1830). Sediment accumulation rates rose sharply between 1940 and 1970 and then leveled off, while P inflows record their largest increases after 1970. The post-1970 rise in P loading reflects higher mean flows in the Mississippi River as well as increasing P concentrations in its waters during the last three decades. The recent increase in TP inferred from our sediment study is consistent with a rising trend in flow-adjusted summer TP measured at the inflow to Lake Pepin from 1977 to 1991 (Heiskary and Vavricka 1993).

Uncertainties

The task of unraveling the sedimentary record of this large riverine basin was not without difficulties. Sediment dating was a particular problem given the extremely high sedimentation rates that severely dilute the atmospheric flux of ^{210}Pb and limit the age to which dates may be reliably extended. Moreover, the flux of ^{210}Pb to different parts of the basin appears to have shifted over time, requiring these radiometric data to be integrated stratigraphically throughout the basin. A full array of dating tools including magnetic susceptibility, LOI, pollen analysis, ^{137}Cs, and ^{14}C, was ultimately needed to synthesize a reliable sediment chronology. Uncertainties remain, especially for older strata, but the various dating markers constrain one another as do the chronologies for individual cores, and the final results appear robust.

Other difficulties included the strong longitudinal gradient in sediment accumulation that required a large number of cores to characterize. The density of cores employed in this study appears to have been sufficient, for the resulting sediment fluxes for the current decade match closely sediment loads determined independently by input/output monitoring. This success can be partially attributed to the unambiguous delineation of the depositional region of the lake, which is defined by a sharp morphometric scarp separating erosional surfaces from those conformably accumulating fine-grained sediment.

Uncertainties also persist in the P mass balance. Diatom reconstructions of lake-water TP concentrations are consistent with measured values for the current decade, but past estimates are less secure. Pre-European values may actually be closer to 30–40 μg l^{-1}, than the 50 μg l^{-1} derived from the diatom models. There are a number of problems with these numerical methods (Anderson 1997; Sayer 2001), not the least of which is the lack of a single regional P model that adequately encompasses the range of diatom assemblages found in the Lake Pepin record. A synthesis of TP optima from several training sets was used to model the Lake Pepin data (a necessary though unconventional approach), and results, especially for the older strata, are sensitive to the optima of a few key taxa. Likewise, discharge records for the Mississippi River at Lake Pepin do not extend to pre-settlement times, and extrapolating mean flows to these older strata could result in substantial error. Two diatom-inference models were used to estimate water-column TP in Lake Pepin, and the difference between these two reconstructions (as a measure of uncertainty) produces a relative error of 5–22% in the modeled TP load to the lake (Fig. 13). However, there is little difference in the trajectory of the two models or the magnitude of increase over time.

Results from this study demonstrate that it is possible to obtain quantitative historical accounts of sediment and nutrient loading in riverine systems from sediment accumulation in impoundments along their courses. Few previous investigations have attempted such a mass-balance approach (Evans and Rigler 1980; Jordan et al. 2001; Moss 1980; Rippey and Anderson 1996), and none has been done on a major watershed the size of the UMR. And because most river impoundments are man-made, the historical records they provide are of generally short duration and do not include pre-impact conditions (Bradbury and Van Metre 1997; Van Metre et al. 1997). Few major rivers possess natural impoundments like Lake Pepin where sediments have accumulated conformably for thousands of years.

Acknowledgments This project could not have been completed without the help of many contributors. We were assisted in all phases of sediment coring by Scott Schellhaass (Metropolitan Council) and in core processing and magnetic susceptibility by Brian Haskell (University of Minnesota). Pollen analysis was done by Barbara Hansen (University of Minnesota), and P analyses were directed by Bill James and John Barko (US Army Corps of Engineers). Cesium-137 dating was done by Dan Steck (St John's University) and GIS mapping was completed by Howard Post (GeoData Model Solutions). Lead-210 dating and sample handling at the St. Croix Watershed Research Station were the responsibility of Kelly Thommes. This work was funded by the Metropolitan Council Environmental Services and ably directed by Kent Johnson as project manager.

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